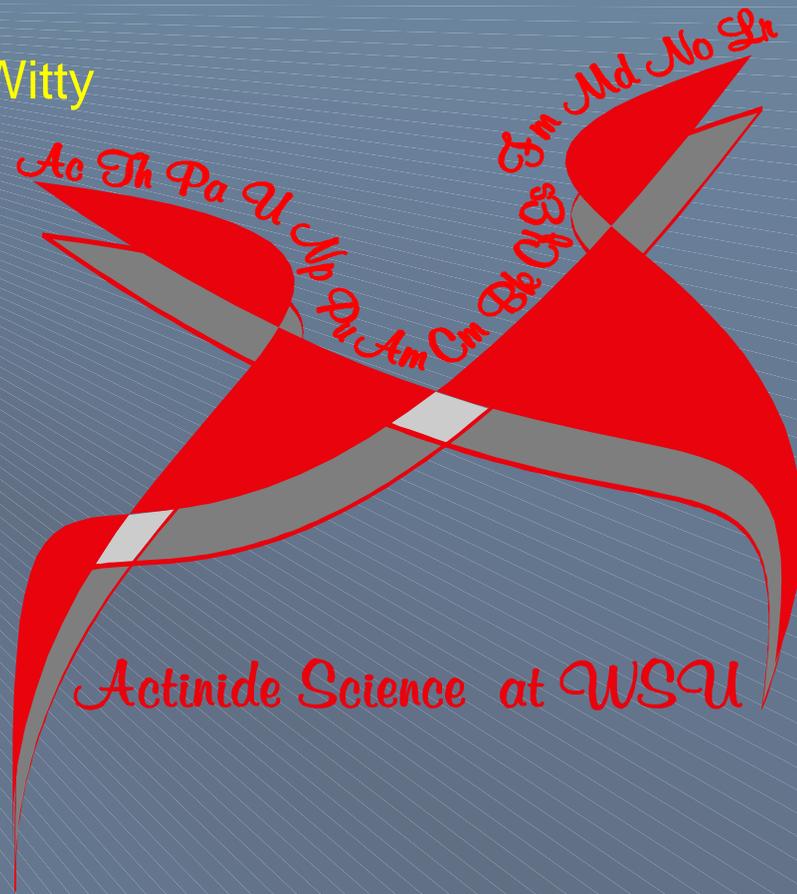


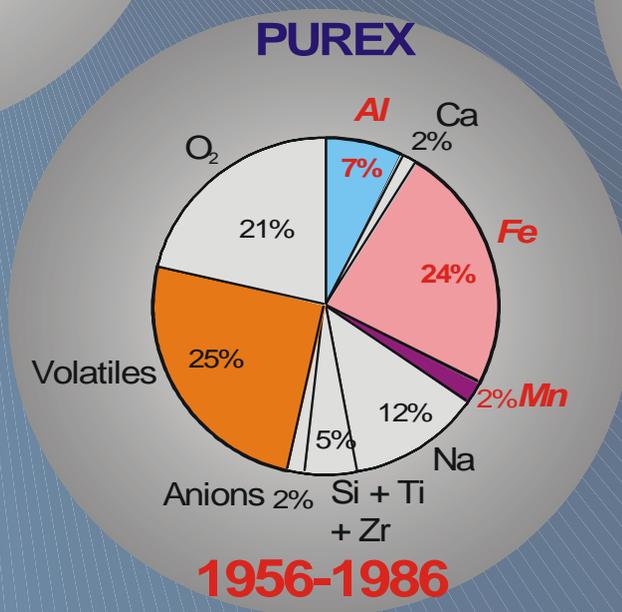
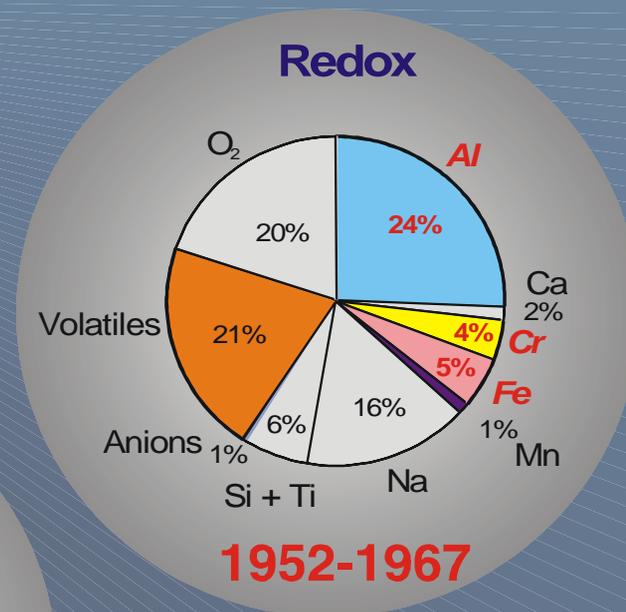
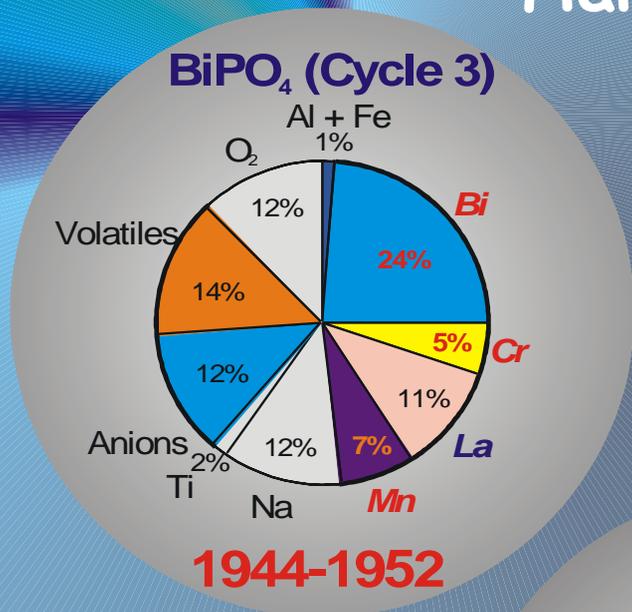
Actinides in alkaline oxidizing media: species relevant to tank waste pretreatment

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Sludge Compositions and Simulant Analyses Hanford Waste Tanks



Volatiles represent primarily organics

O₂ represents the residue needed for mass balance

Waste Glass Limiting Species

Al: **Redox** > **PUREX** >> **BiPO₄**
 Cr: **BiPO₄** > **Redox** >> **PUREX**
 P: **BiPO₄** >> **PUREX** > **Redox**

Sludge Washing Procedure

Consecutive washing of sludges was performed in order to determine if actinide ions are likely to be mobilized during the component-wise dissolution of the sludge matrix (parallel also for U)

Class I - Basic Simulation Washing Solutions

- 0.01 M NaNO_2 + 0.01 M NaOH (sluicing liquid from Hanford baseline strategy)
- 3.0 M NaOH (leachant from Hanford baseline strategy)
- H_2O

Class II - Exploratory Washing Solutions

- 0.05 M Glycolic Acid + 0.10 M NaOH
- 0.10 M HNO_3
- 2.0 M HNO_3
- 0.50 M 1-Hydroxyethane-1,1-diphosphonic acid (HEDPA)

Class II leaches designed to learn “preferred associates” of actinides in sludges

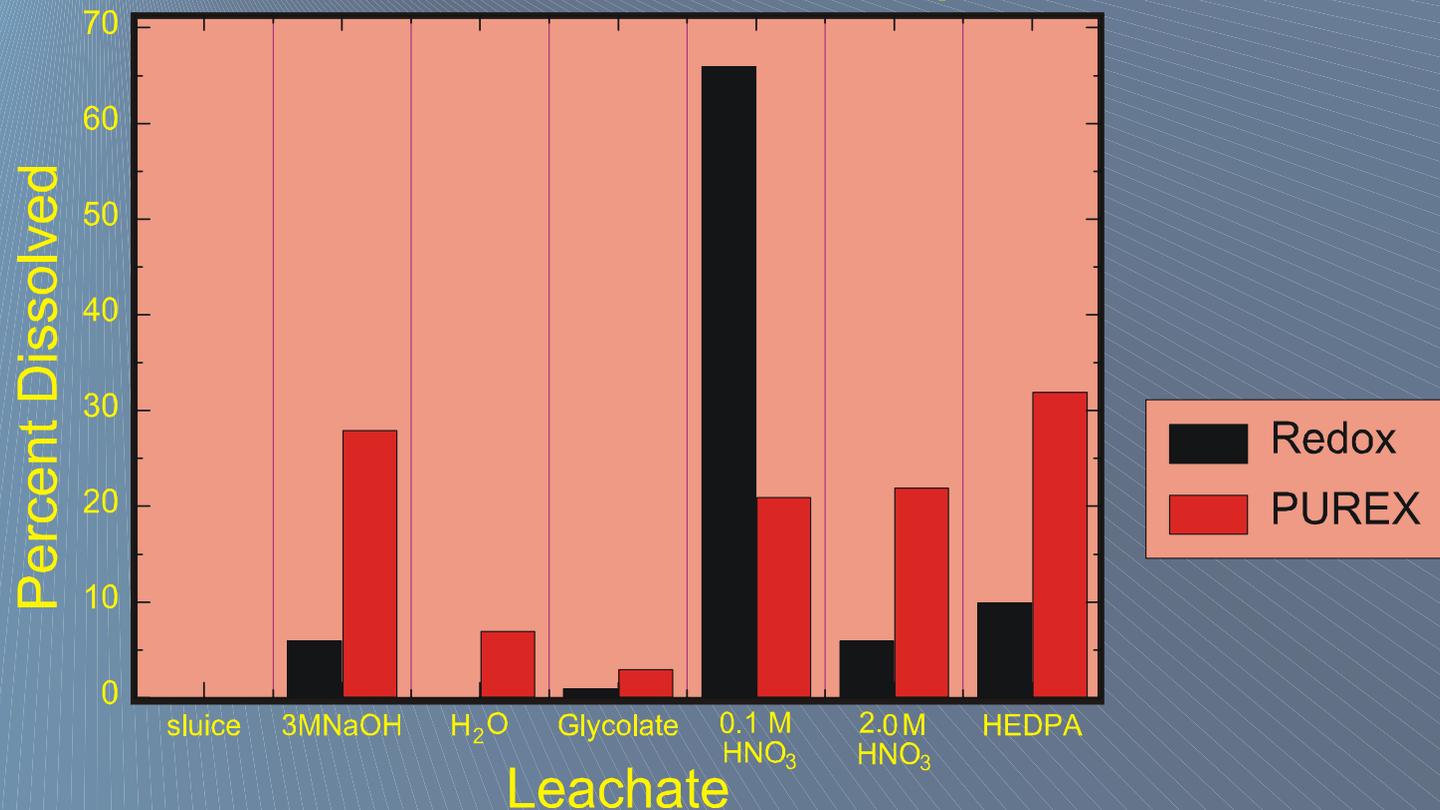
Observations and Correlations from First Stage Investigations

- ✧ Baseline sludge wash (3.0 M NaOH) results in incomplete removal of Cr, P, Al from sludge simulants - Different results for different sludge types (BiPO₄, Redox, PUREX)
- ✧ Cr, P, and Al removal can be increased with acid contact
- ✧ More aggressive (acids/chelating agents) treatments have varied impact on actinide mobility
- ✧ Pu and Am dissolution low in baseline sludge wash - U and Np dissolution is not negligible in baseline
- ✧ Symmetrical anionic oxy-hydroxides dominate Np speciation in 1-5 M base but...
- ✧ Chelating agents alter speciation of actinides in strong base
- ✧ Speciation of U, Np, Pu oxide/hydroxides are not identical in strong base
- ✧ Uranium species in sludge simulants are different
- ✧ Oxidative scrubs (e.g., to enhance Cr removal) likely to shift actinides to higher oxidation states

Sludge Washing Observations III (What about Al and P?)

From BiPO_4 sludge simulant, about 10 % of P (each) is removed in 3.0 M NaOH and 2.0 M HNO_3 leaches

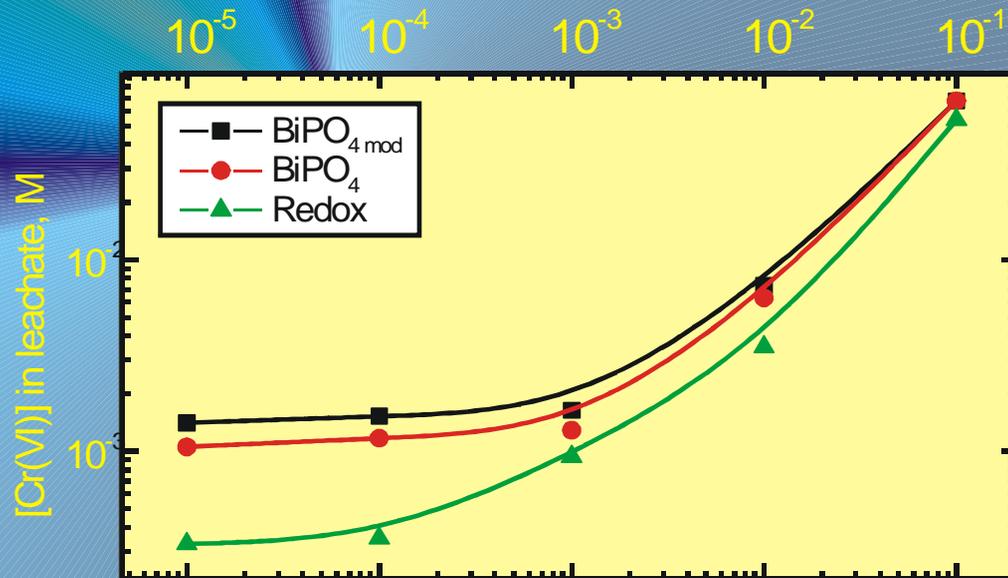
Aluminum Removal from Sludge



Observations and Correlations from First Stage Investigations

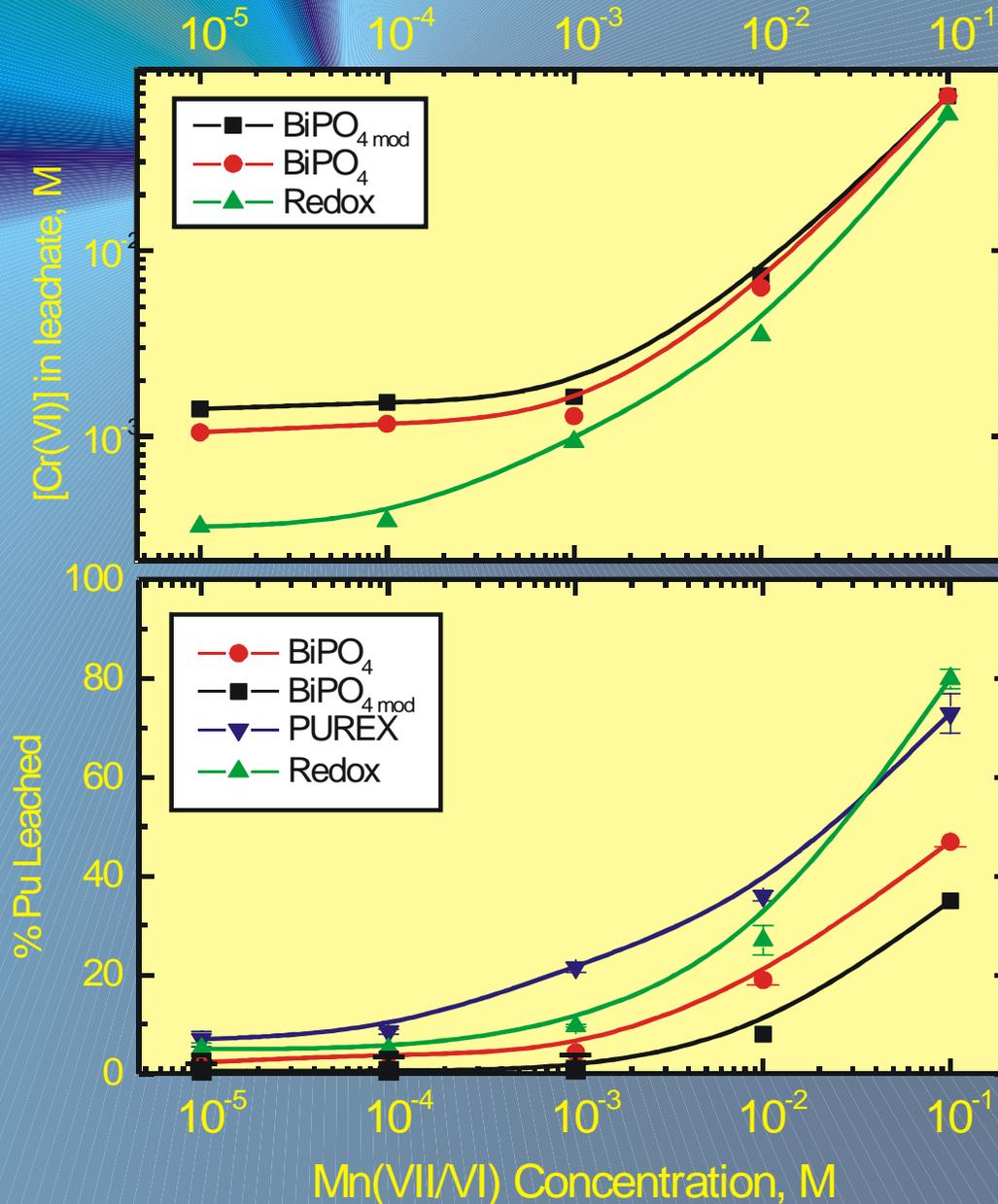
- ☆ Baseline sludge wash (3.0 M NaOH) results in incomplete removal of Cr, P, Al from sludge simulants - Different results for different sludge types (BiPO₄, Redox, PUREX)
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Permanganate Oxidation of Sludge Simulants



Chromium leaching from sludge simulants by permanganate in 3.0 M NaOH increased above a threshold value

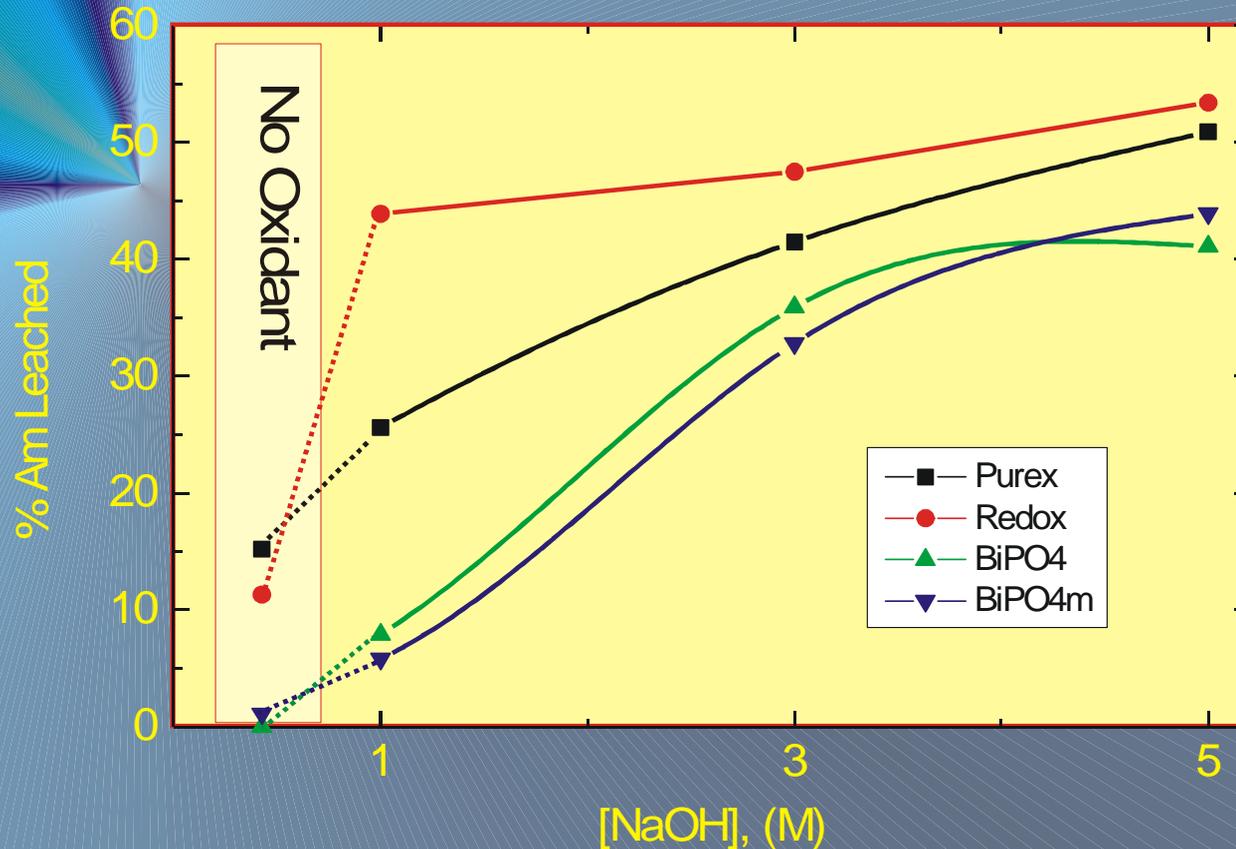
Permanganate Oxidation of Sludge Simulants



Chromium leaching from sludge simulants by permanganate in 3.0 M NaOH increased above a threshold value

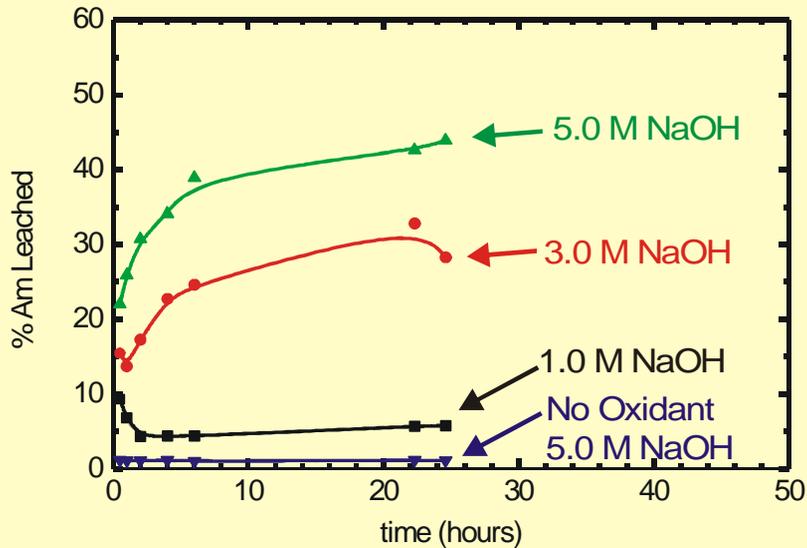
Plutonium in the supernate increases in parallel

Americium Leaching Increased in Alkaline Oxidative Treatment

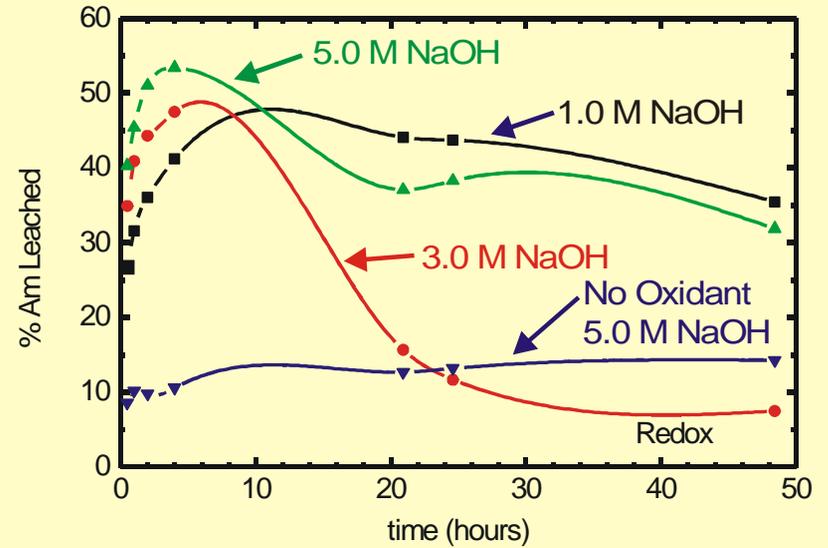


- Am leach rates increase in the order $\text{BiPO}_4 < \text{REDOX} < \text{PUREX}$
- Persulfate and permanganate have similar effect on Am mobility
- Most probable Am species is Am(V)
- Am(V) not be stable indefinitely, but will persist while the oxidant is present

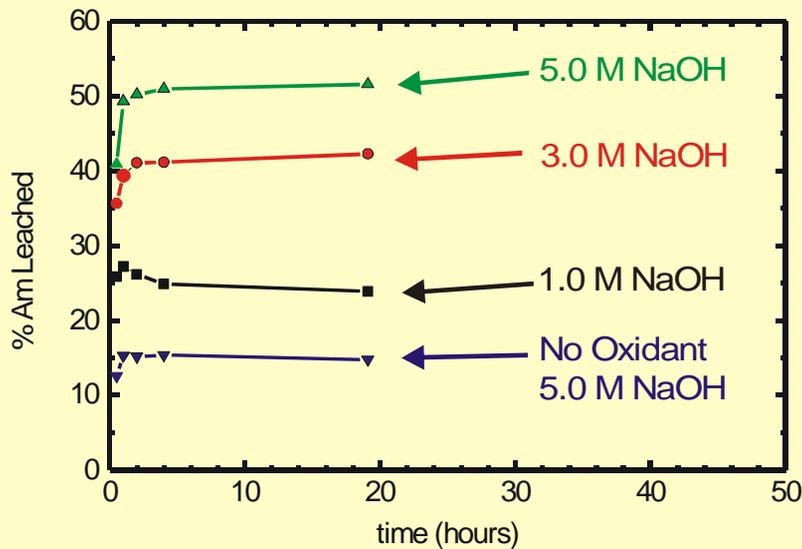
Am Leached by Persulfate from BiPO₄



Am Leached by Persulfate from Redox



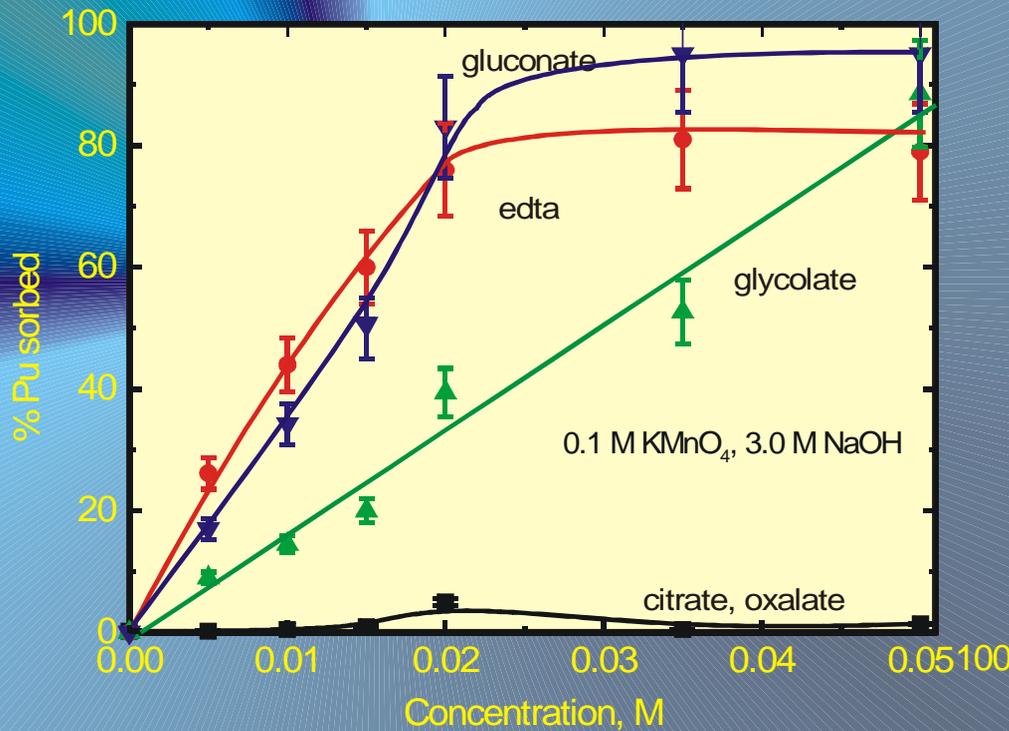
Am Leached by Persulfate from PUREX



- Relative rates of Am(III) oxidation
- Note that Am(V) not long-term stable (except in the presence of holding oxidant)
- More Am is (oxidized) and leached at higher base concentration

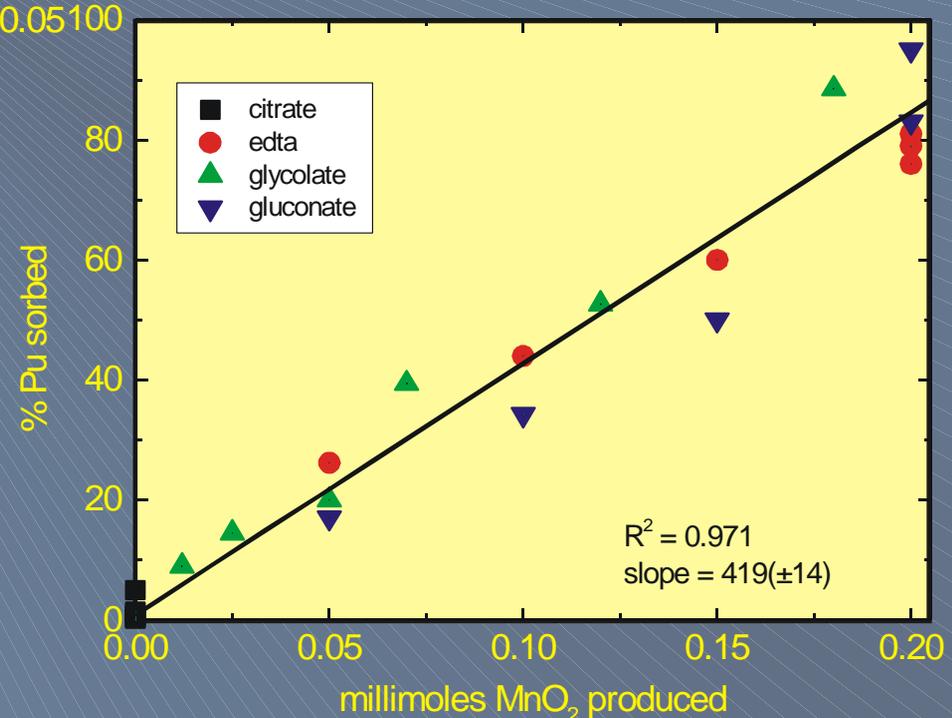
Plutonium Sorption to MnO₂ as Organics are Oxidized

Conditions of experiments:
No sludge, 60k cpm/ml ²³⁸Pu



Observations:

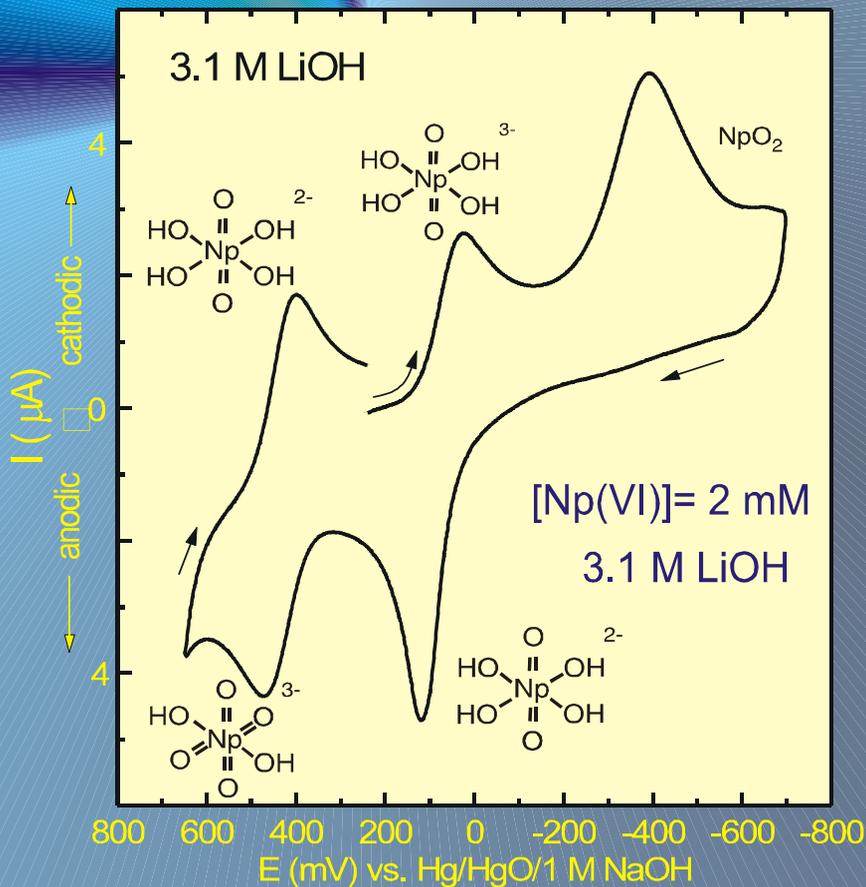
- Plutonium sorption onto MnO₂ product correlates linearly with the amount of MnO₂ present
- edta, gluconate @ high conc does not redissolve Pu from MnO₂
- Neither citrate nor oxalate are oxidized under these conditions



Observations and Correlations from First Stage Investigations

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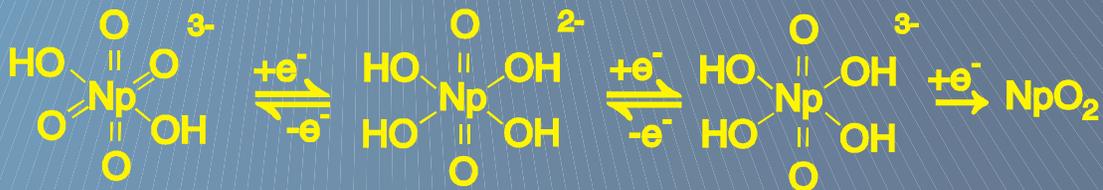
Cyclic voltammogram of Np(VI) in 3.1 M LiOH on the Pt electrode, first scan. Scan rate 20 mV/s



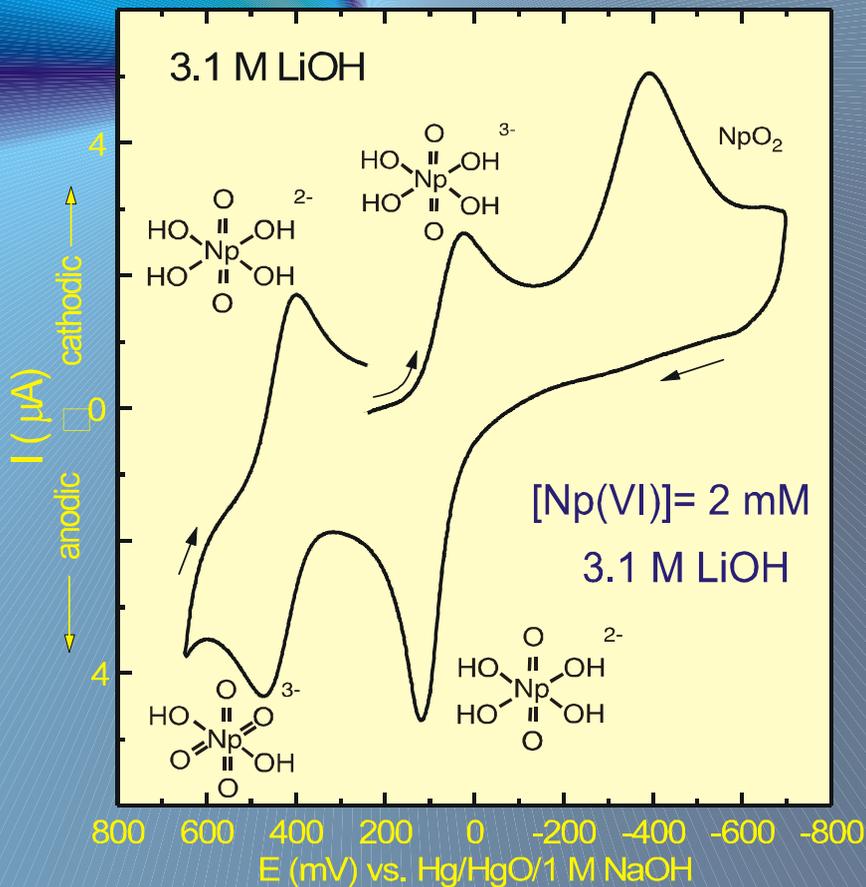
Electrochemical reversibility becomes less common as the carbonate concentration increases

Np(V)-Np(VI) couples quasi-reversible in basic 1 M NaOH sodium oxalate solutions (thermodynamic data in the literature do not explain this observation)

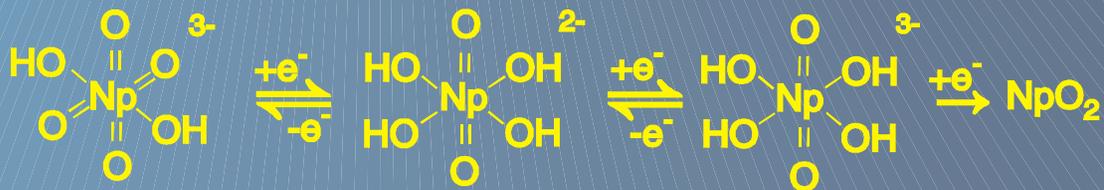
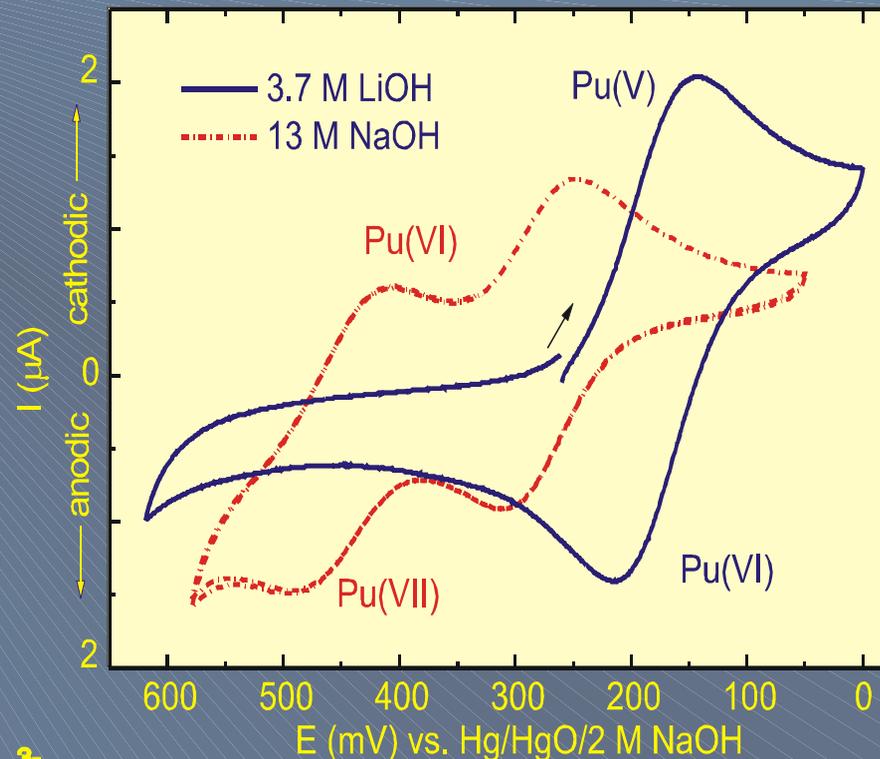
More complex speciation indicated in EDTA containing basic solutions (thermodynamic data in the literature do not explain this observation)



Cyclic voltammogram of Np(VI) in 3.1 M LiOH on the Pt electrode, first scan. Scan rate 20 mV/s



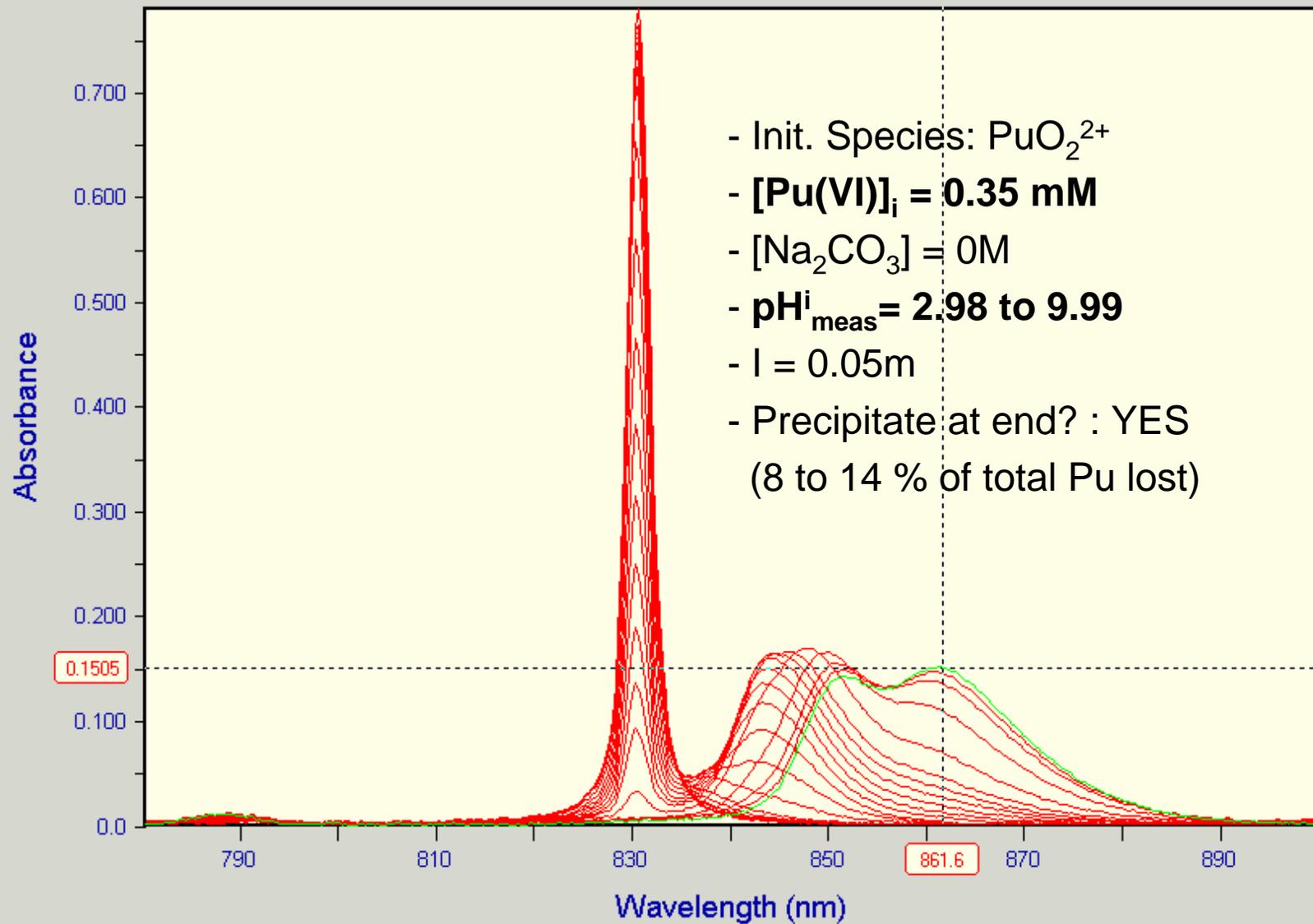
Cyclic voltammograms of Pu in 3.7 M LiOH and 13 M NaOH



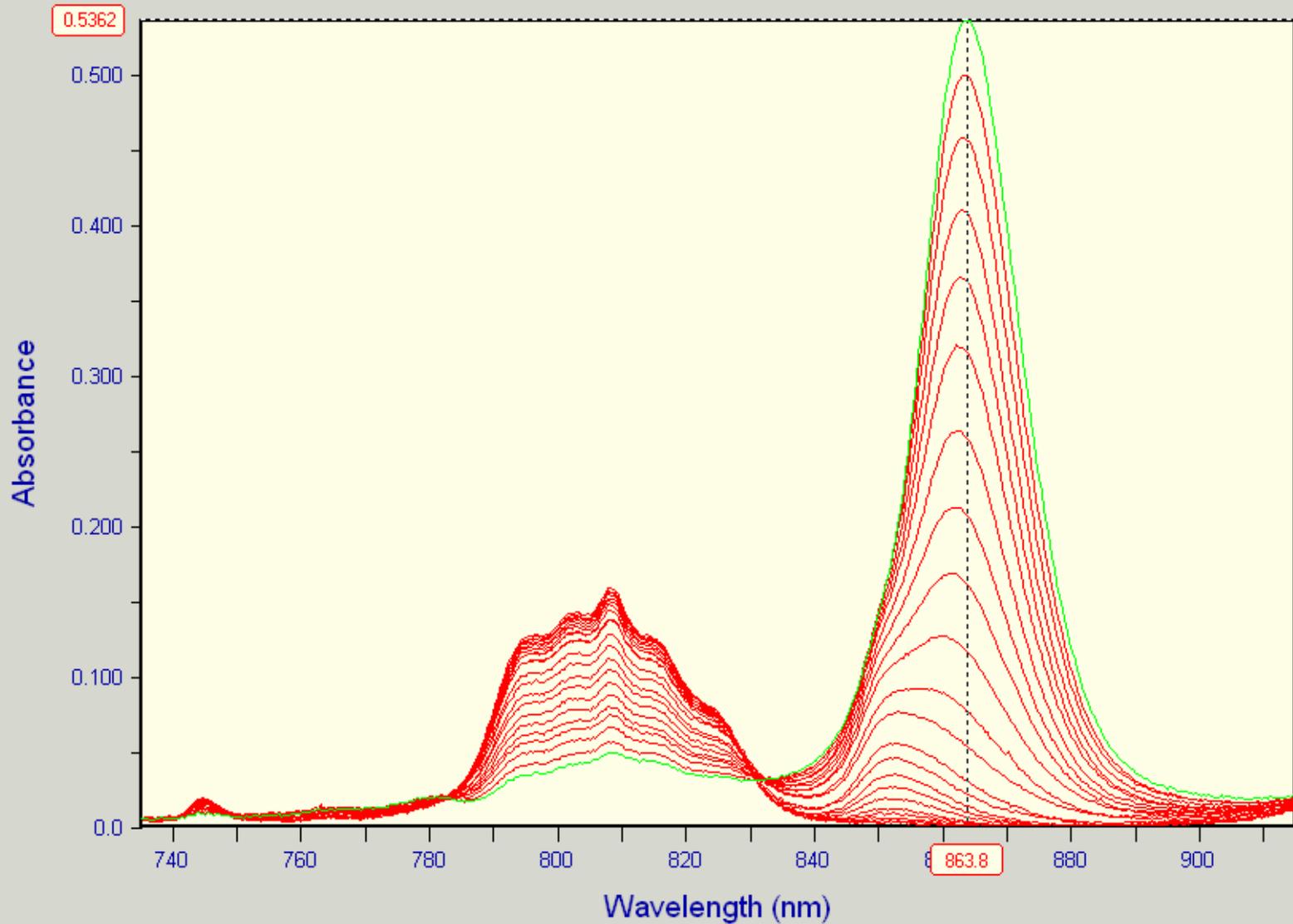
Pu(VI) in alkaline media:

- Study motivated by the treatment of the alkaline radioactive wastes at the Hanford Site.
 - Identification of Pu(VI) species in alkaline media is not straightforward and literature still presents some discrepancies among the data.
 - Species accepted in the OECD database^[1]:
 $\text{PuO}_2\text{CO}_{3(\text{aq})}$, $\text{PuO}_2(\text{CO}_3)_2^{2-}$, $\text{PuO}_2(\text{CO}_3)_3^{4-}$,
 $(\text{PuO}_2)_3(\text{CO}_3)_6^{6-}$, $\text{PuO}_2(\text{OH})^+$, $\text{PuO}_2(\text{OH})_{2(\text{aq})}$ and
 $(\text{PuO}_2)_2(\text{OH})_2^{2+}$.
 - Search for new species, specifically those species that might exist in the “no-man’s land” between $\text{PuO}_2(\text{CO}_3)_3^{4-}$ and $\text{PuO}_2(\text{OH})_4^{2-}$.
- [1] OECD-NEA, Chemical Thermodynamics of Np and Pu, Elsevier publisher, Vol. 4, 2001.

Experiment 1: $\text{PuO}_2^{2+} + \text{OH}^-$



Experiment 5: $\text{PuO}_2^{2+} + \text{CO}_3^{2-} + \text{OH}^-$:



1-Hydroxyethane-1,1-diphosphonic acid (HEDPA)

Powerful chelating agent widely used in industrial applications

A potential leachant for enhancing aluminum oxide dissolution

Known to complex actinides in acidic aqueous solutions

Characterization of uranyl complexes with HEDPA conducted using these techniques:

- ┆ Potentiometric titration
- ┆ Calorimetry
- ┆ NMR spectroscopy
- ┆ UV-visible spectrophotometry
- ┆ Electrospray mass spectrometry

Results indicate stable uranyl complexes are formed over a wide range of pH

Gluconic acid as a complexant

- ▮ $pK_a = 3.6$ (similar to glycolic acid), lactones appear in acidic solutions
- ▮ Weak complexing agent in acidic media (comparable to glycolic acid up to pH 4-5)
- ▮ Useful complexant for a variety of polyvalent metal ions in alkaline solutions (suppresses Fe^{3+} , Al^{3+} , UO_2^{2+} hydrolysis and precipitation of metal hydroxides) - widely applied industrially, including at Hanford
- ▮ Stoichiometry of thermodynamically-stable polyvalent metal complexes often described as MH_nL , implying deprotonation of alcoholic groups in the presence of metal cations
- ▮ Multiple metal oxygen bonds and polynuclear complexes are commonly seen in the literature
- ▮ Thermodynamically speaking, MH_nL cannot be distinguished from $M(OH)_nL$

Experimental

^{13}C NMR – Alcoholic protons are very weak acids – additional studies indicate that uranyl cation interacts with carboxylate, 2-OH and 4-OH groups but not with 3-, 5-, or 6- hydroxy groups.

UV-vis – Spectral features change with pH and metal-ligand ratio but indicate the simultaneous presence of several different species.

Potentiometric titration - Titrations carried out in triplicate and at various ratios of U(VI):gluconate identify M(L) , M(OH)L , and $\text{M}_2(\text{OH})_2\text{L}$ species and allow calculation of complexation equilibrium constants.

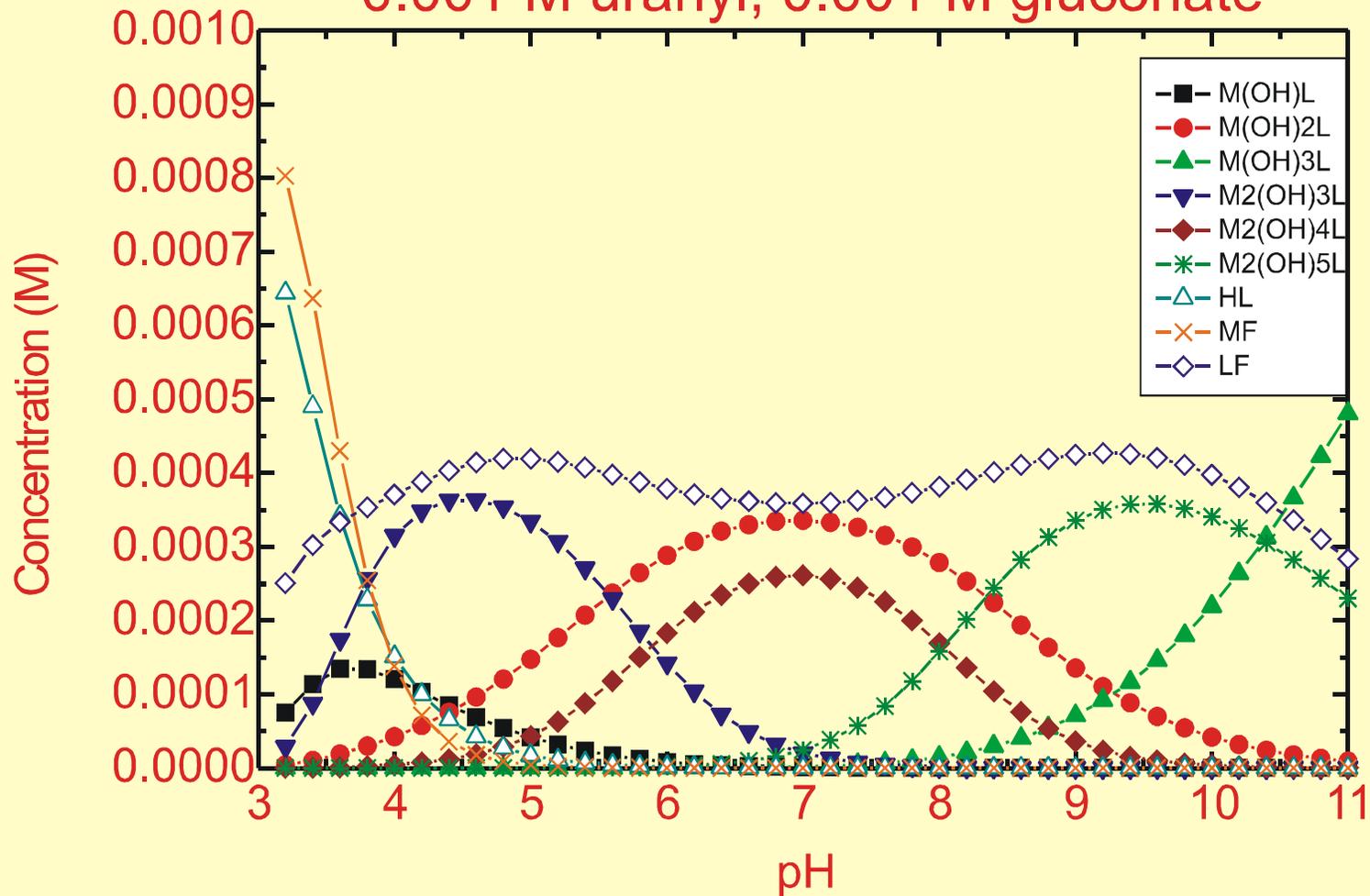
Calorimetry - Heats of dimer-monomer conversion determined by titration calorimetry

Computational Modeling – Most probable structure of monomer and dimer complexes can be rationalized consistent with experimental results

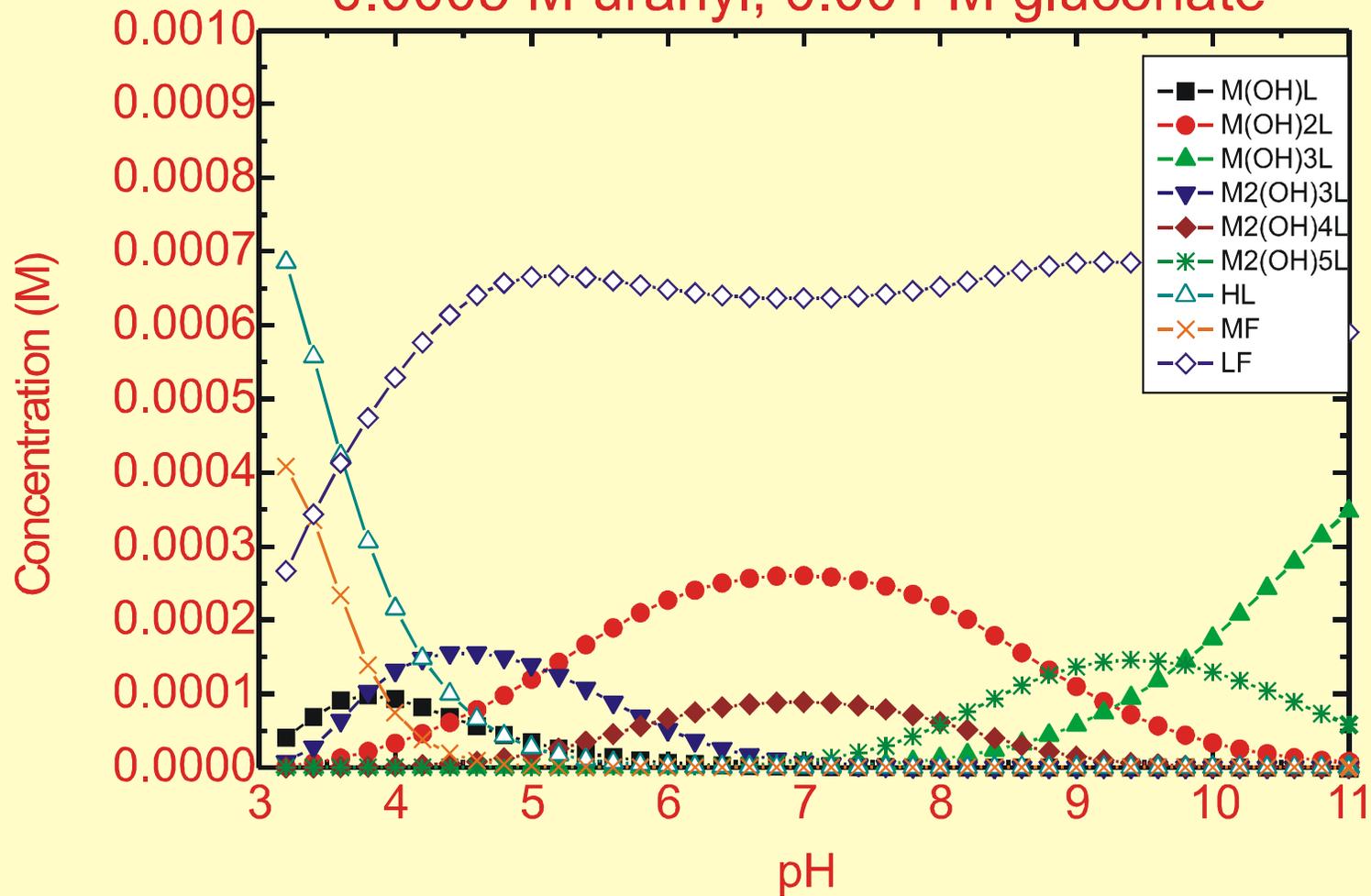
The best fit of the potentiometric titration data required six species of the general stoichiometry $[(\text{UO}_2)_{1-2}(\text{OH})_{2-5}(\text{Gluc})_1]^{-2-0}$.

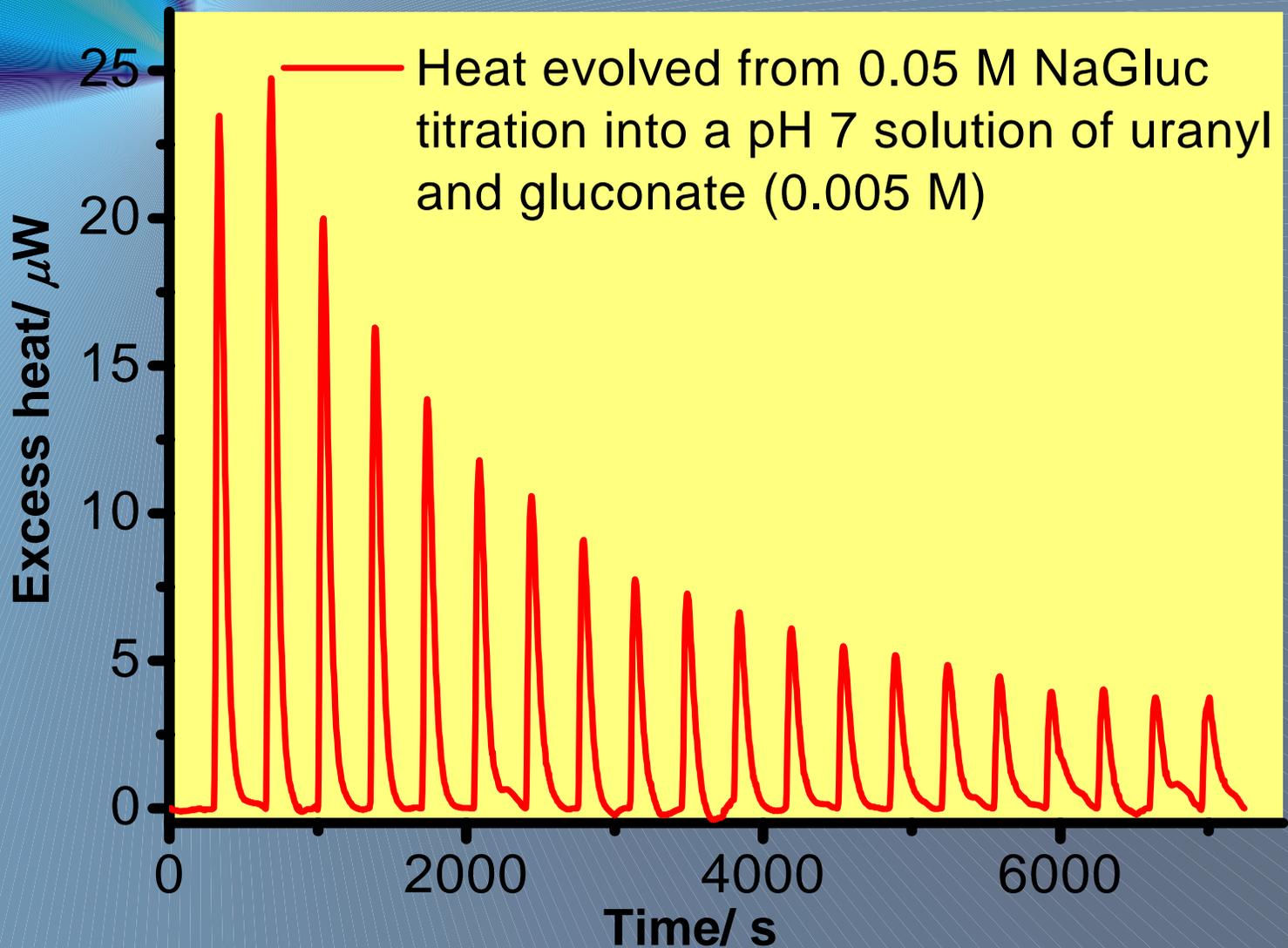
Stoichiometry <i>mhl</i>	Log β_{mhl}	$\pm 1 \sigma$
1, -1, 1	-0.63	0.07
1, -2, 1	-5.08	0.03
1, -3, 1	-14.36	0.03
2, -3, 1	-4.35	0.03
2, -4, 1	-10.24	0.05
2, -5, 1	-18.27	0.04

0.001 M uranyl, 0.001 M gluconate

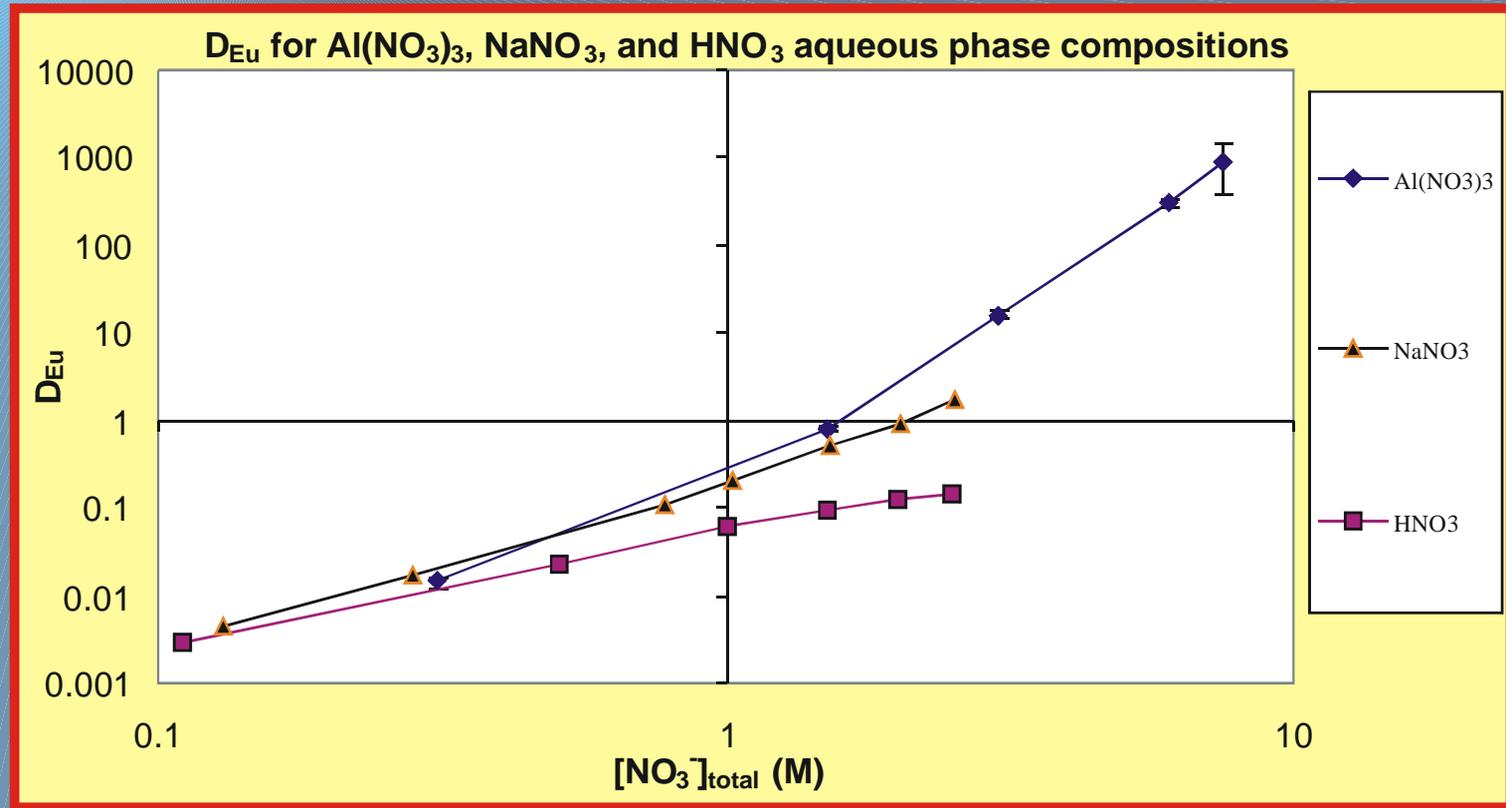


0.0005 M uranyl, 0.001 M gluconate





Cleanup of residual radioactivity from acidic $\text{Al}(\text{NO}_3)_3$ by solvent extraction



Summary Oxidative Leaching

- ▮ Permanganate/manganate, persulfate equally powerful oxidants
- ▮ They oxidize everything - Cr, actinides, organics, but oxalate and citrate are resistant in alkaline solutions (they do oxidize in acid)
- ▮ Product MnO_2 appears to assist with control of actinide solubility (waste glass limit for Mn is 4%)
- ▮ Different performance with respect to actinide mobilization in different sludge types, i.e., correlates with Cr content
- ▮ Caution needed to assure that the manganate/permanganate are not applied in excess of the amount needed for Cr(III) oxidation
- ▮ Some readily oxidizable organics (e.g., gluconate) might be judiciously applied to control actinide solubility if excess permanganate/manganate is applied in oxidative sludge washing

New Information on Actinide Solution Species in Alkali

- ‖ $\text{NpO}_2(\text{OH})_4^{2-/3-}$ dominant species of Np in strongly basic solutions
Np(IV)/Np(V), Np(V)/Np(VI), Np(VI)/Np(VII) potentials measured in 3.0 M base - edta and maybe oxalate alter this speciation
- ‖ $\text{PuO}_2(\text{OH})_4^{2-/3-}$ species are similar, but potentials are significantly different than for Np, altering the relative stability of species
- ‖ U(VI) complexes with malonate and oxalate are significant in neutral pH, less important in concentrated base
- ‖ U(VI) complexes with HEDPA (1-hydroxyethane-1,1-diphosphonic acid) are soluble in strongly basic media - thermodynamic parameters determined
- ‖ New Pu(VI) mixed hydroxycarbonate complexes identified spectrophotometrically in the pH region between stability fields of $\text{PuO}_2(\text{CO}_3)_3^{4-}$ and $\text{PuO}_2(\text{OH})_4^{2-}$
- ‖ Polynuclear uranyl gluconate complexes exist - thermodynamics parameters developed - new insights to structural chemistry

Acknowledgments

- ▮ Mark Jensen (ANL/CHM) consultation on many diverse aspects of this project
- ▮ Andrew H. Bond (Postdoc, ANL) for the sludge simulant synthesis, characterization, and the leaching experiments.
- ▮ Artem Guelis (Postdoc, ANL) for the Np Electrochemistry
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- ▮ Alex Garnov (Postdoc, LBNL) Am, U leaching studies
- ▮ Wendy Reed (Postdoc, LBNL) leaching studies, thermodynamics
- ▮ Ivan Laszak (Visiting Scientist, ANL) Oxidative leaching studies, Pu speciation in alkaline carbonate solutions
- ▮ Giselle Sandi (ANL/CHM), Professor Petr Vanysek (Chemistry Department, Northern Illinois University) for help in the organization of the electrochemistry experiments
- ▮ Carrying on the Work: Postdoc Leigh Martin (WSU), Postdoc Brian Powell (LBNL), Graduate Students Ryan Harrington (WSU) Undergraduate Students Jim Neeway, Rob Olsen, Ryan Witty (WSU)

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